

THE ANALYSIS OF LIQUIDS FROM COAL CONVERSION PROCESSES

By

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INTRODUCTION

Major coal-conversion processes under consideration (1) for development by U.S. interests are capable of producing a wide variety of products. Processing and using these materials in future applications will require a better understanding of their composition than has been necessary with conventional energy sources. To provide basic data, the Bartlesville Energy Research Center has been studying liquid products derived from various coal-conversion processes.

Depending upon the material to be processed and the information desired, numerous approaches to appropriate characterization may be taken. Some investigators have used mass spectrometry as a single technique to analyze materials of wide boiling range without prior separations (2,3). These mass spectral methods are well conceived and furnish useful information, but cannot provide the compositional detail that is possible with prior separations. Further, more accurate type assignment and quantitation are possible with preliminary separations. Limited analytical data that provide physical characteristics (4) such as percent oil, asphaltenes, gravity, viscosity, etc. may be satisfactory for monitoring coal liquefaction process operations and for comparing materials that will satisfy utility type fuel requirements. However, the composition of coal liquids to be further upgraded such as those to be used for transportation, needs to be determined in more detail to provide the refiner with the necessary basis for processing these materials.

The Bartlesville Energy Research Center is using the approach of physical and chemical separation, followed by instrumental characterization, to provide considerable detailed data on the composition of coal liquefaction products. The key to the identification procedure for those materials boiling above 200° C lies in the GPC-mass spectral correlation method developed at Bartlesville (5,6). Most of the procedures used were developed for the analysis of high-boiling petroleum fractions during a cooperative project between the U.S. Bureau of Mines and the American Petroleum Institute (7). Some minor modifications have been necessary to adapt the procedures to the products of coal liquefaction.

Materials from three different coals and two liquefaction processes were studied: two COED materials produced from Utah and western Kentucky coals and a third material from the Synthoil process using West Virginia coal. The COED process involves pyrolysis of the coal followed by catalytic hydrogenation of the crude liquid, whereas the Synthoil process is a direct catalytic hydrogenation of coal slurried in a recycle liquid. Although process conditions are not available for the two COED products, the Synthoil product was prepared by processing the coal at 450° C and 4,000 psig (8). Hydrogen and a slurry of 35 percent coal in recycle oil were fed at 25 pounds per hour into a nominally half-ton (slurry) per-day unit with a 14.5-foot-long catalytic reactor. The catalyst was 1/8-inch pellets of cobalt molybdate on silica alumina. Two other liquid products from the H-Coal process are under current investigation, and will be completed soon.

EXPERIMENTAL

The general procedure used in the study of full-boiling-range coal liquid products is shown in Figure 1. Boiling ranges of distillates were checked by simulated distillation (9) to establish the approximate boiling ranges desired. In previous work with petroleum crudes, care was exercised to prepare distillates having identical boiling ranges so that more precise comparisons of data could be made. However, smaller samples of the available coal liquids have precluded adjustment of still conditions to any great extent, and the boiling ranges as determined by simulated distillation for the distillates prepared are not exactly the same. This was not considered essential for these initial studies because the primary interest was to determine whether the procedure might be effective and the adjustments necessary to make an effective characterization. All distillates were prepared in a 4-inch-diameter Rota-Film molecular still. The still, a continuous-flow, wiped-well vessel, provides minimum residence time of the sample at elevated temperatures, thus limiting thermal degradation of the material being processed. Material is passed through the still for each set of conditions of temperature and pressure at the rate of 600 to 1,000 ml/hr.

After the distillates were prepared, the material boiling below about 200° C was separated further into acids, bases, and hydrocarbon-neutral fractions for analysis by gas chromatography (GC), ultraviolet (UV) fluorescence, and mass spectrometry. Distillates boiling from about 200° C to 370° C and 370° C to 540° C were processed through adsorption columns (10) to produce four concentrates for each distillate: saturates, monoaromatics, diaromatics, and polyaromatic-polar material. The saturates were analyzed directly by mass spectrometry; monoaromatics and diaromatics were separated by gel permeation chromatography (GPC) and analyzed by GPC-mass spectral correlations (5,6); and the polyaromatic-polar concentrate was separated into acids, bases, and hydrocarbon-neutrals. The polyaromatic-polar concentrate less acids and bases was then separated by GPC and characterized in the same manner as the monoaromatics and diaromatics.

The adsorption columns used were about 8 feet long by 1 inch diameter, packed with 28 to 200 mesh, Davison grade 12 silica gel in the top half and 80 to 200 mesh Alcoa F-20 alumina in the bottom half, and were operated downflow. The GPC column was about 16 feet long by 1 inch diameter, packed with 100Å polystyrene gel in the top half and 400Å polystyrene gel in the bottom half, and was operated downflow. The mass spectrometer used for these studies was a CEC 21-103C low-resolution instrument; saturates were analyzed by high-ionizing voltage spectra and aromatics by low-ionizing voltage spectra. High-resolution mass spectrometers, the AEI MS-30 and CEC 110, were also used to resolve certain heteroatomic species that overlapped the same nominal hydrocarbon series. NMR spectra from a Varian A-60 instrument were obtained to determine the proton distributions across the GPC runs and thereby confirm and enhance the findings of the GPC-mass spectral correlations.

RESULTS AND DISCUSSION

Summary data shown in Tables I and II were selected from comprehensive characterization studies (11-13) that have been completed for each coal liquid. Table IA summarizes distillate distributions, Table IB shows totals for major compound classes, and Table II lists ring number distributions by compound class for each distillate. As shown by the distillate distributions data in Table IA, the Synthoil material from West Virginia coal is the highest boiling of the three, having 95.6 percent boiling above about 200° C and 25.7 percent residuum (boiling above about 540° C). Utah syncrude is rated second in higher-boiling material with 85.7 percent boiling above about 200° C. Western Kentucky shows 78.4 percent boiling above 200° C.

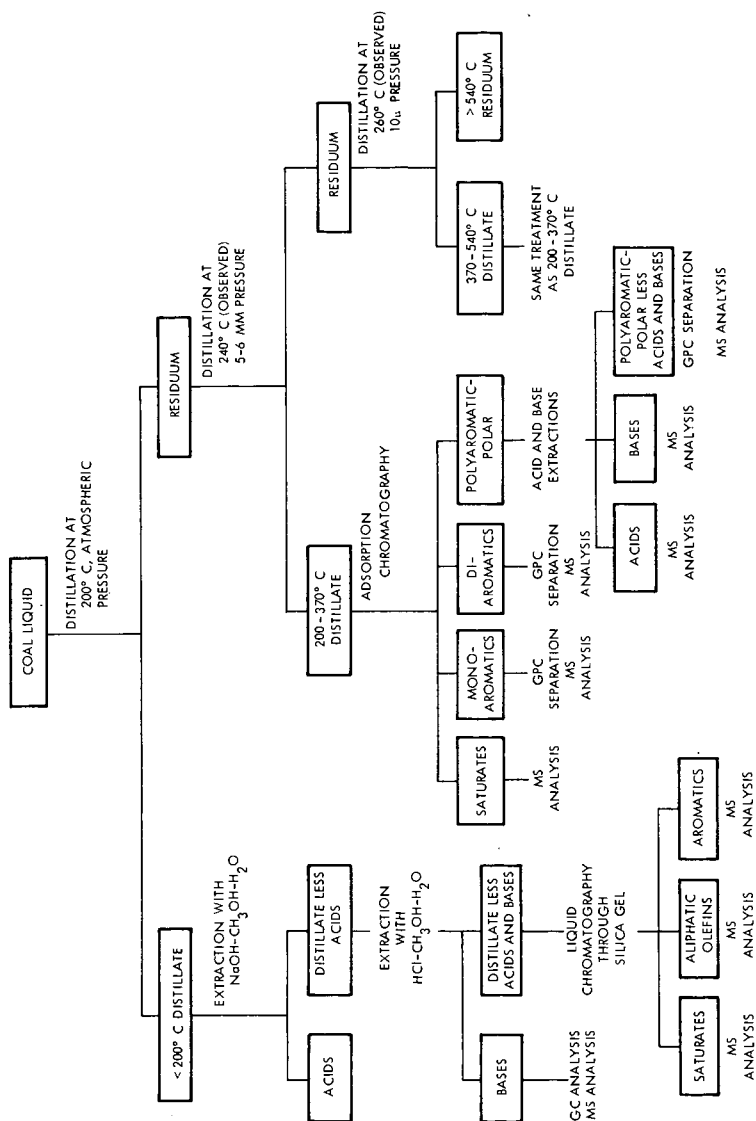


FIGURE 1. Procedure for Characterizing Coal Liquids.

TABLE I
DISTILLATES AND MAJOR COMPOUND TYPES SEPARATED
FROM THREE COAL LIQUIDS

A. COAL LIQUIDS AND DISTILLATES

	COED Syncrude Utah Coal	COED Syncrude Western Kentucky Coal	Synthoil West Virginia Coal
	Wt. Pct.	Wt. Pct.	Wt. Pct.
COAL LIQUIDS:			
Sulfur	0.05	0.08	0.42
Nitrogen	0.48	0.23	0.79
DISTILLATE DISTRIBUTIONS:			
< 200° C Distillate ¹	13.3	21.0	4.4
200 - 370° C Distillate ²	45.4	54.2	42.6
370 - 540° C Distillate ³	40.3	24.2	27.3
540° C+ Residuum ⁴	-	-	25.7
Losses	1.0	0.6	-

B. MAJOR COMPOUND TYPE DISTRIBUTIONS

Total Saturates	30.10	33.42	10.65
Total Monoaromatics	20.06	33.64	14.23
Total Diaromatics	14.41	12.77	15.53
Total Polyaromatics	14.48	7.91	14.61
Heteroatomic Species	1.50	0.29	2.24
Acids	8.17	3.11	10.40
Bases	1.30	1.05	2.75
Residuum (Not Analyzed)	None	None	25.7
Other Material Not Analyzed	9.98	7.81	3.89
Totals	100.00	100.00	100.00

¹ < 204° C for Utah, < 205° C for western Kentucky, and < 207° C for Synthoil.

² 204 - 381° C for Utah, 205 - 380° C for western Kentucky, and 207 - 363° C for Synthoil.

³ 381° C+ residuum for Utah, 380° C+ residuum for western Kentucky, and 363 - 531° C for Synthoil.

⁴ Utah and western Kentucky syncrudes had no material boiling above about 540° C.

TABLE II
RING NUMBER DISTRIBUTIONS OF HYDROCARBON CONCENTRATES FROM THREE COAL LIQUIDS

Concentrate and total number of rings determined (includes Aromatic and Aliphatic rings)	Syn crude From COED Process				Syn crude From COED Process				Synthoil Liquid Product From West Virginia Coal			
	Utah Coal		381° C +		Western Kentucky Coal		380° C +		< 207° C		207-363° C	
	Distillate	Distillate	Residue	Distillate	Distillate	Distillate	Residue	Distillate	Distillate	Distillate	Distillate	Distillate
Saturates:												
Paraffin	-	4.06	4.67	-	2.79	1.47	-	1.09	-	-	-	0.78
1-ring	-	1.39	1.09	-	3.34	1.00	-	1.71	-	-	-	0.91
2-ring	-	1.65	0.50	-	3.22	0.67	-	1.59	-	-	-	0.17
3-ring	-	1.11	1.09	-	2.41	0.75	-	1.52	-	-	-	0.23
4-ring	-	1.58	0.67	-	1.37	0.69	-	0.89	-	-	-	0.26
5-ring	-	2.85	1.11	-	0.40	0.53	-	-	-	-	-	0.31
6-ring	-	-	1.30	-	-	0.44	-	-	-	-	-	-
TOTALS	7.05	12.64	10.41	14.34	13.53	5.55	1.19	6.80	-	-	-	2.66
MONOAROMATICS:												
1-ring	-	1.09	0.66	-	1.76	0.28	-	0.21	-	-	-	0.09
2-ring	-	4.50	0.60	-	7.83	0.39	-	0.90	-	-	-	0.05
3-ring	-	3.91	0.88	-	8.43	0.80	-	4.75	-	-	-	0.09
4-ring	-	1.52	1.60	-	3.56	2.11	-	4.62	-	-	-	0.23
5-ring	-	0.41	1.33	-	1.04	1.38	-	1.15	-	-	-	0.42
6-ring	-	0.01	0.55	-	0.19	0.69	-	0.02	-	-	-	0.35
7-ring	-	-	0.16	-	-	0.32	-	-	-	-	-	0.10
8-ring	-	-	0.05	-	-	0.11	-	-	-	-	-	0.04
TOTALS	2.79	11.44	5.83	4.75	22.81	6.08	1.21	11.65	-	-	-	1.37

TABLE II--continued

RING NUMBER DISTRIBUTIONS OF HYDROCARBON CONCENTRATES FROM THREE COAL LIQUIDS

Concentrate and total number of rings determined (includes Aromatic and Aliphatic rings)	Syncrude From COED Process Utah Coal			Syncrude From COED Process Western Kentucky Coal			Synthoil Liquid Product From West Virginia Coal		
	381° C +			380° C +			363-531° C		
	<204° C Distillate	204-381° C Distillate	Residuum	<205° C Distillate	205-380° C Distillate	Residuum	<207° C Distillate	207-363° C Distillate	363-531° C Distillate
Weight Percent of Total Liquid Product									
DIAROMATICS:									
2-ring	-	3.82	0.31	-	2.06	0.08	-	3.21	0.05
3-ring	-	3.41	0.91	-	3.11	0.72	-	3.98	0.64
4-ring	-	1.11	1.80	-	1.46	1.69	-	1.68	1.51
5-ring	-	0.28	1.53	-	0.31	1.63	-	0.34	1.22
6-ring	-	-	0.77	-	0.06	0.98	-	0.01	1.17
7-ring	-	-	0.34	-	0.01	0.47	-	-	0.99
8-ring	-	-	0.13	-	tr	0.16	-	-	0.36
9-ring	-	-	-	-	-	0.04	-	-	0.16
10-ring	-	-	-	-	-	-	-	-	0.05
11-ring	-	-	-	-	-	-	-	-	0.02
TOTALS	-	8.62	5.79	-	7.00	5.77	0.14	9.22	6.17
POLYAROMATICS:									
3-ring	-	0.80	1.14	-	1.11	0.37	-	0.83	0.20
4-ring	-	1.29	2.36	-	1.07	1.04	-	1.48	1.45
5-ring	-	0.75	2.88	-	0.42	1.20	-	0.79	1.42
6-ring	-	0.26	3.32	-	0.21	1.04	-	0.15	2.03
7-ring	-	0.11	1.56	-	0.09	1.15	-	0.08	2.20
8-ring	-	-	0.01	-	0.02	0.16	-	0.03	2.01
9-ring	-	-	-	-	-	0.03	-	0.02	1.03
10-ring	-	-	-	-	-	-	-	0.01	0.69
11-ring	-	-	-	-	-	-	-	0.01	0.18
TOTALS	-	3.21	11.27	-	2.92	4.99	-	3.40	11.21

Table 1B shows some indication of the degree of aromaticity for each syncrude. For example, assuming the 25.7 percent residuum shown for Synthoil is mostly aromatic, Synthoil then would be the most aromatic of the three having a total aromatic hydrocarbon content near 70 percent, whereas western Kentucky and Utah syncrudes are about 54 percent and 49 percent, respectively.

The quantities of sulfur and nitrogen determined for each coal liquid shown in Table 1A and the amounts of acids, bases, and saturates listed in Table 1B reflect, to some extent, the degree of hydrogenation for each product. For example, the data suggest that the western Kentucky COED product probably was more severely hydrogenated than the Utah COED product, although coal structure or other processing conditions could account for some of the differences in composition. No direct comparison of the Synthoil product with the COED products could be made because of the substantial differences in processing as well as the coal source.

Further insight can be gained into the cyclics present in the hydrocarbon structures of the three coal liquids by examination of the data in Table 11. From the data on saturates, note the lower concentrations of total paraffins as compared to total cyclics. For the Utah syncrude, total paraffins in the saturates amount to about 8.7 percent of the syncrude and cyclics about 14.3 percent, which means the total saturates are about 63 percent cyclic. Western Kentucky syncrude saturates show about 4.3 percent of the syncrude as total paraffins and 14.8 percent as cyclics, or about 78 percent of the saturates are cyclic. The Synthoil product saturates show a paraffin content of 1.9 percent of the total liquid and cyclics content of 7.6 percent, giving an approximate value of 80 percent cyclics in the saturate concentrates. Since Utah syncrude and western Kentucky syncrude were produced by the same process, the significant difference in the amount of paraffins produced would indicate some possible differences in the structures of the coal sources, although the lack of details on the processing of both coals makes this observation tentative. From the distributions shown in Table 11, the aromatics which contain four or more total rings add up to about 23.1, 22.6, and 14.4 percent of the Utah syncrude, western Kentucky syncrude, and Synthoil product, respectively. These data would indicate that the Utah and western Kentucky syncrudes may contain more of the larger aromatic ring systems than the Synthoil product; however, as shown in Table 1B, 25.7 percent of the Synthoil product is residuum that was not analyzed (and probably is composed of multi-ring systems), and about 13.2 percent of the product is in acids and bases. Total ring number distributions shown for each major compound class indicate the two-, three-, four-, and five-ring systems to be predominant in all three syncrudes, Synthoil having material up to 11 total rings. Mass spectral and GPC correlation data and NMR data for these materials indicate structures somewhat more condensed, with more short alkyl groups attached to the cyclic nucleus, than those found in similar boiling ranges of petroleum (14-18). We expect to establish soon the amount of condensation and structural arrangement of materials in the GPC fractions to provide more useful information on the cyclic structures for determining proper refining processes.

CONCLUSIONS

In general, the scheme followed in separation of syncrude materials for characterization studies has provided data for determining appropriate refining processes for these materials. The preliminary separations provide more meaningful fractions for accurate analysis by mass spectrometry and other instrumental techniques by type identification and quantification. The refiner should find this type of data useful in the selection and development of processes for upgrading coal liquids to finished products.

For the three materials examined, Synthoil product appears to be the most aromatic, with ring systems having up to about 11 total rings. Differences between the two COED syncrudes

may be attributable to the severity of hydrogenation of the crude pyrolysis liquids, although insufficient information is available to distinguish between the effects of process conditions and character of coal used as raw material. In continued studies, the characterization and analysis of additional liquids from known combinations of coal source, liquefaction process, and degree of upgrading will provide a more meaningful basis for future refining processes. For more meaningful data, future studies will require access to information such as the coal source and process conditions.

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